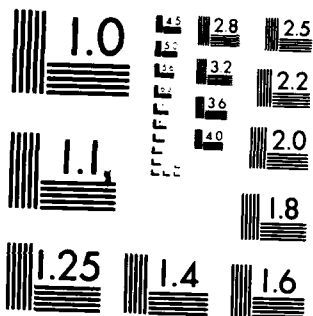AD-A131 300   EXCITED-STATE PROCESSES OF RELEVANCE TO   1/1
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by

Arthur B. Ellis

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The excited-state properties of semiconductor electrodes play a crucial role in photoelectrochemistry. Luminescence offers a means for characterizing the electronic structure and excited-state decay routes of semiconductors employed in PECs and underscores their relationship to electrochemistry: PL can be perturbed and EL initiated by charge-transfer events occurring at the semiconductor-electrolyte interface.

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The ability of a semiconductor to serve as both photoreceptor and electrode in photoelectrochemical cells (PECs) highlights the importance of the semiconductor's electronic structure and excited-state deactivation routes in the construction of such devices. Characterization of these semiconductor properties and their perturbation by an electric field is greatly aided by spectroscopic methods. Although this paper deals primarily with one such method – luminescence – reference will also be made to complementary spectroscopic techniques.

Luminescent properties of semiconductors provide information analogous to that obtained for molecular systems. The spectral distribution, for example, can be used to characterize electronic structure in the sense of identifying the states involved in the emissive transition; the efficiency and lifetime of the luminescence can provide valuable information on the kinetics of excited-state processes. Moreover, examination of luminescent properties under various experimental conditions – different temperatures, applied voltages, e.g. – can be used to evaluate the susceptibility of the semiconductor's electronic structure and excited-state kinetic scheme to environmental perturbation. An appreciation of these effects has played a significant role in the development of luminescent semiconductors for use as phosphors and light-emitting diodes (LEDs), to name a few applications (1,2).

Luminescence from semiconductors may be produced by a number of methods. The most common is absorption of photons which either directly or indirectly populates the emitting excited state and results in photoluminescence (PL). Electroluminescence (EL), in which the excitation results from an electric current, has also been studied extensively. Other methods include excitation by a beam of electrons, cathodo-luminescence, and by mechanical means, triboluminescence. This paper is

confined to PL and EL properties. Sections below provide an overview of

PL properties, a description of their perturbation in a PEC, and a discussion

of the complementary information obtained from EL properties.

PL Properties

Scheme I presents features of the electronic structure of a semiconductor which

are of relevance to PL. The key event initiating PL is the absorption of a photon;

Scheme I. Electronic Structure of a Semiconductor Electrode
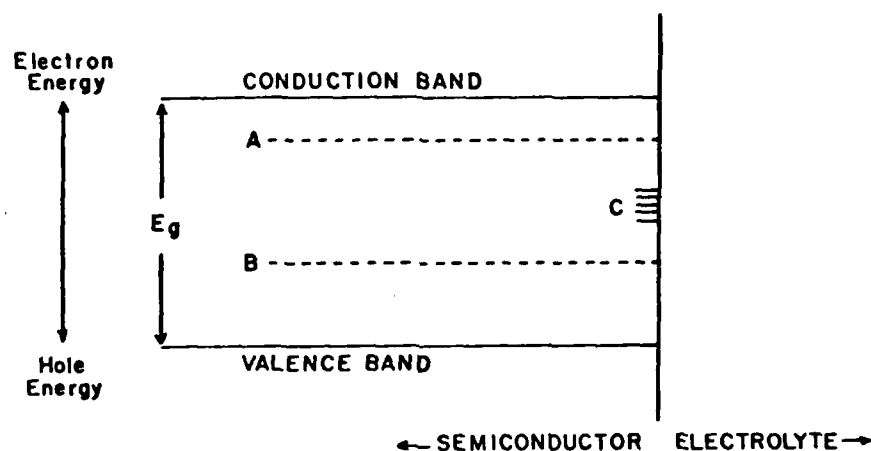
efficient absorption generally requires photons whose energies exceed the

band-gap energy of the semiconductor, E_g. The absorption of such an ultraband-

gap photon promotes an electron from the valence band to the conduction band,

concomitantly forming a valence-band hole. This electron-hole ($e^- - h^+$) pair

can be regarded crudely as a "one-electron" picture of the semiconductor's

excited state and is pictured in Scheme II.

Luminescence arises from the radiative recombination of $e^- - h^+$ pairs. There

are several recombination mechanisms which will give rise to PL at energies very

near E_g, sometimes called edge emission (3). In addition to resulting from

recombination of a free conduction band electron, e^-_{CB}, and valence band hole, h^+_{VB},

edge emission also occurs when electrons and/or holes are trapped in states

near the band edges prior to recombination. Excitons represent another source of

edge emission (3-5). A free exciton is a Coulombically-bound $e^- - h^+$ pair which has

been modelled by analogy to the hydrogen atom as possessing hydrogenic-like states whose energies lie near E_g. Bound excitons, in which the e^- or h^+ is associated with a defect site, may also contribute to edge emission. However, because of their low binding energies, excitonic contributions to PL are usually most significant at low temperatures.

As energies of states arising from lattice imperfections move away from the band edges, subband-gap PL may occur from the recombination of electrons or holes trapped in these deeper states. The imperfections may arise from impurity atoms or native defects such as interstitial atoms or vacancies. Scheme I depicts such bulk intraband gap states by the labels "A" and "B". The states labelled "C" in Scheme I are confined to the (near-)surface region of the semiconductor and may also participate in radiative transitions leading to subband gap emission. These surface states, as they are called, may play an important role in mediating the transfer of charge across the semiconductor-electrolyte interface and are discussed in more detail below.

Although radiative recombination has been the focus of discussion thus far, its companion process, nonradiative recombination, plays an equally important role in excited-state deactivation; nonradiative recombination leads to heat via lattice vibrations. Scheme II depicts radiative and nonradiative recombination with rates denoted by k_r and k_ℓ, respectively. In the absence of photocurrent, the competition between the two kinds of recombination determines the radiative quantum efficiency, ϕ_r, and the lifetime of the excited state, τ. The physical significance of these quantities is analogous to their description for molecular systems with ϕ_r representing the steady-state ratio of photons emitted to photons absorbed and τ representing the longevity of the excited state, as determined from the time-resolved decay of PL following pulsed excitation (6).

Scheme II. Excited-State Deactivation Pathways of a
Semiconductor Electrode[a]

—SEMICONDUCTOR ELECTROLYTE—
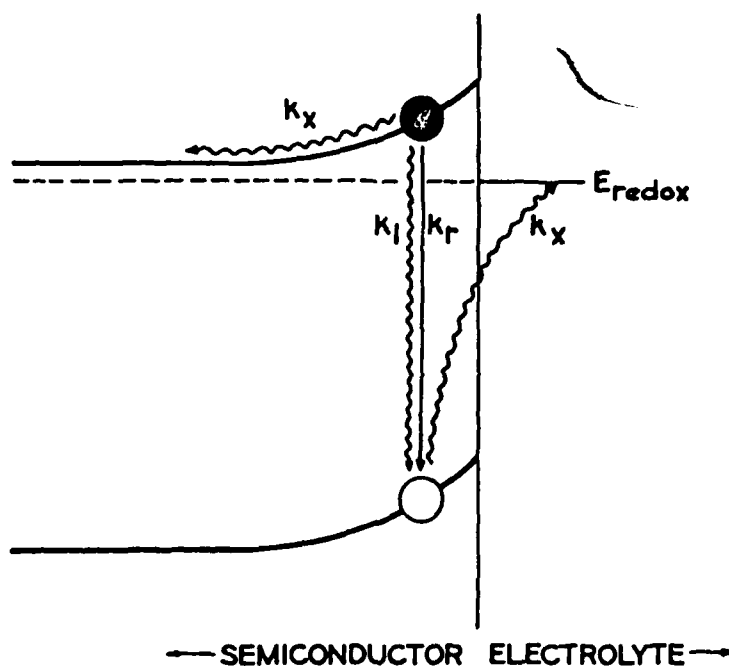
[a]The filled and open circles represent an electron and hole,

respectively. Wavy and solid arrows correspond to nonradiative

and radiative decay paths, respectively. The dashed line near

the conduction band indicates the semiconductor's chemical

potential or Fermi level; under dark, equilibrium conditions

this potential matches that of the electrolyte, denoted by

E_{redox}. Intraband gap states which might play a role in the

various decay routes have been omitted for simplicity.

It is important to note that in many cases k_ℓ and k_r of Scheme II will not be

the simple unimolecular rate constants which are associated with numerous

molecular systems and which permit the formulation of ϕ_r and τ as $k_r(k_r+k_{nr})^{-1}$

and $(k_r+k_{nr})^{-1}$, respectively. The complexity of excited-state kinetics can

be illustrated by the decay of PL for phosphors which often follows a power-law

rather than an exponential dependence, presumably reflecting the role of

intraband gap trapping states in the kinetic scheme (1).

PL Properties in a PEC

The use of a semiconductor as an electrode in a PEC introduces photocurrent as a third competitive excited-state deactivation mechanism; the additional form of nonradiative decay is represented by "k_x" in Scheme II. As indicated in Scheme II, photocurrent arises from the separation of $e^- - h^+$ pairs, a process facilitated by an electric field formed upon immersion of the semiconductor in an electrolyte (7). The electric field is symbolized in the scheme by the parallel bending of valence and conduction band edges in the region near the semiconductor surface; the zone over which band-bending occurs, typically $\sim$0.1-1 μm in width, is called the depletion region. For the n-type semiconductor which is pictured, the direction of the electric field is such that the semiconductor serves as a photoanode.

The effects which the passage of photocurrent has on PL properties have been examined with a number of n-type semiconductors exhibiting edge emission and/or impurity-based subband-gap emission. The former category includes ZnO and CdS_XSe_{1-X} $(0 \leq X \leq 1)$ samples; in the latter category are Cu-doped ZnO (ZnO:Cu) and CdS:Te (8-11). In all cases examined, passage of anodic photocurrent from ultraband-gap excitation quenched the PL intensity but did not appreciably alter the spectral distribution. This effect is illustrated for CdSe edge emission in the left-hand panel of Figure 1: As more positive potentials are applied to the n-type semiconductor and band bending is increased (7), the PL intensity uniformly diminishes throughout the band. Since the spectral distribution of impurity-based PL is independent of potential, it may be inferred that the intraband gap states involved in the transition bend in parallel with the conduction and valence band edges.

The potential dependence of photocurrent and PL can be measured simultaneously with the latter monitored at a single wavelength (12). Data for a CdSe-based PEC are presented in the right-hand panel of Figure 1 and illustrate the tug-of-war between $e^- - h^+$ pair separation and recombination: With increasingly positive potentials, greater electric fields enhance photocurrent and diminish PL. The degree of PL quenching for these steady-state experiments can be roughly predicted

by a simple model which treats ϕ_r, ϕ_x (photocurrent quantum efficiency, i.e.,

electrons in the circuit per photons absorbed), and ϕ_{nr} (quantum efficiency for

nonradiative recombination) as the only excited-state decay routes: $\phi_r + \phi_x + \phi_{nr} = 1$

(9). As the potential is increased from open circuit, where $\phi_x = 0$ and the PL

efficiency is ϕ_{r_o}, to an in-circuit potential characterized by ϕ_x and ϕ_{r_1}, the

fraction of $e^- - h^+$ pairs diverted to photocurrent (ϕ_x) is the fraction prevented

from recombining and the fraction by which PL intensity is quenched, eq. (1).

$$\frac{\phi_{r_o}}{\phi_{r_1}} = \frac{1}{1-\phi_x} \qquad (1)$$

Implicit in this argument is the assumption that the ratio of ϕ_r to ϕ_{nr} is

independent of potential. A complementary technique, photothermal spectroscopy

(PTS), has recently been employed to monitor the related conversion of light

to heat with potential (13). For a ZnO:Cu-based PEC, ϕ_x was determined by PTS, by

PL quenching, and by a direct measurement (photocurrent resulting from measured

input power); good accord was found in comparing the three techniques (11).

Reasonable agreement between direct measurements of ϕ_x and its determination

by eq. (1) was also obtained for PECs based on $CdS_X Se_{1-X}$ ($0 \leq X \leq 1$) and

CdS:Te (9,10). For CdS:Te which exhibits both edge emission (2.4 eV; λ_{max} ~510 nm)

and PL due to a Te-bound exciton (~2.0 eV; λ_{max} ~600 nm), rough agreement was

also observed at several different excitation wavelengths for which optical

penetration depths and ϕ_{r_o} values were different, and at several temperatures

where ϕ_{r_o} and the spectral distribution of PL were different (9,14,15).

The temporal characteristics of PL have thus far received relatively little

attention in the context of a PEC, yet they might potentially provide a means

for integrating the kinetics of interfacial charge-transfer processes into the

excited-state kinetic scheme. Among the difficulties which have hampered such

studies are the time constants associated with conventional electrochemical

circuitry. However, new techniques for circumventing this problem such as

coulostatic-flash methods are being investigated in conjunction with temporal

PL measurements (16,17).

EL Properties

The initiation of luminescence by interfacial charge-transfer events is a
useful complement to PL studies. EL has been observed for a number of n-type
semiconductors using aqueous, alkaline peroxydisulfate electrolytes (10,18-23).
The three-step mechanism proposed for EL in this medium is illustrated in
Scheme III (20-22). In the first step, the ability of n-type semiconductors to
serve as dark cathodes at potentials cathodic of their flat-band potential (the
potential at which band bending is absent) is exploited in the reduction of

Scheme III. Proposed Mechanism for EL in Peroxydisulfate
Electrolyte[a]

$$S_2O_8^{2-} + e_{CB}^- \longrightarrow SO_4^{2-} + SO_4^-$$

$$SO_4^- \longrightarrow SO_4^{2-} + h_{VB}^+$$
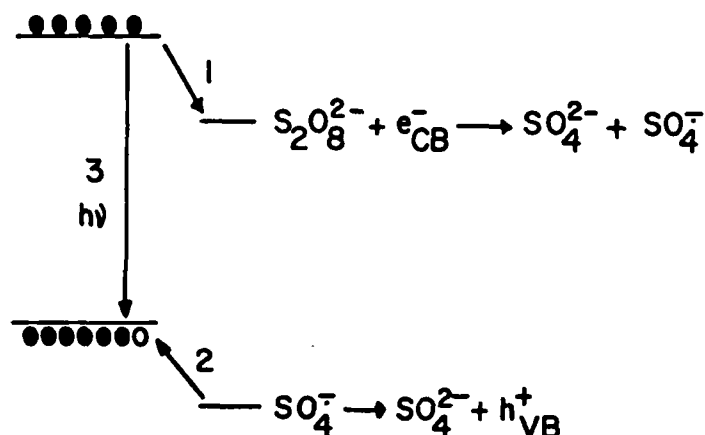
[a]Mechanism proposed in references 20-22.
Filled and open circles represent electrons
and holes, respectively.

$S_2O_8{}^{2-}$ to yield the highly oxidizing sulfate radical anion; some evidence for
competitive electrode reduction, a process which has been probed by reflectance
and photoacoustic spectroscopies, has also been presented (22,24,25). The crucial step
in Scheme III is the second in which SO_4^- injects a hole into (removes an electron from)
the valence band. In the final step, an electron recombines with the injected hole to
yield emission. Should recombination involve electrons and holes at or near the
conduction and valence band edges, respectively, edge emission will be observed;
subband-gap EL will obtain if the electrons and/or holes recombine from intraband
gap states.

Comparisons of PL and EL have been made for several n-type semiconductor electrodes with the general result that bands observed in PL spectra are also observed in EL spectra (10, 18-20). This indicates that the emitting excited state populated in PL experiments is also populated in EL experiments. For a number of semiconductors, however, some subband-gap EL bands had no PL counterparts. These bands have been proposed to originate from transitions involving surface states (10,18-20). That EL might be a more surface-sensitive probe of recombination is not unreasonable in the sense that it is initiated at the semiconductor-electrolyte interface; in contrast, excitation wavelengths used to induce PL will typically have penetration depths exceeding 10^{-5} cm. Other evidence that, on average, EL originates from nearer the semiconductor surface than PL comes from the shape of the emission bands: Discrepancies between PL and EL spectra for several CdS_xSe_{1-x} samples are consistent with greater self-absorption of the emitted light in the PL experiment (10,26).

Another interesting comparison is afforded by the efficiencies of PL and EL. The efficiency of EL, ϕ_{EL}, can be defined as photons emitted per holes injected. By analogy to the phenomenon of electrogenerated chemiluminescence (27), ϕ_{EL} may also be expressed as the product $\phi_{ES}\phi_r$, where ϕ_{ES} is the efficiency of populating the emitting excited state by hole injection (excited states populated per holes injected) and ϕ_r is the emissive quantum efficiency (photons emitted per excited states populated). Direct comparison of ϕ_r and ϕ_{EL} for edge emission bands have been made for CdS_xSe_{1-x} electrodes and yielded similar values of $\sim 10^{-5}$ to 10^{-3} (10). Although the comparison must be qualified by consideration of the different spatial zones involved in PL and EL, the similar values do suggest that ϕ_{ES}, the efficiency with which the emitting excited state is populated in EL, is very high and perhaps approaches its maximum value of unity for these systems.

Conclusion

The excited-state properties of semiconductor electrodes play a crucial role in photoelectrochemistry. Luminescence offers a means for characterizing the electronic structure and excited-state decay routes of semiconductors employed in PECs and underscores their relationship to electrochemistry: PL can be perturbed and EL initiated by charge-transfer events occurring at the semiconductor-electrolyte interface.
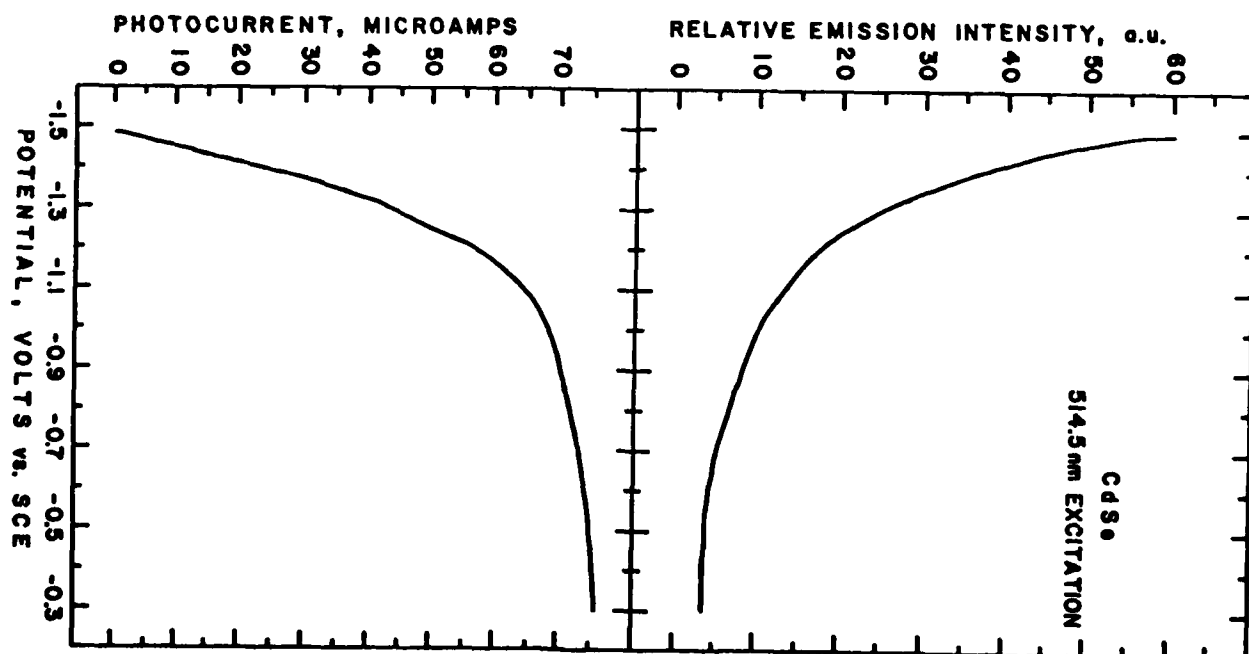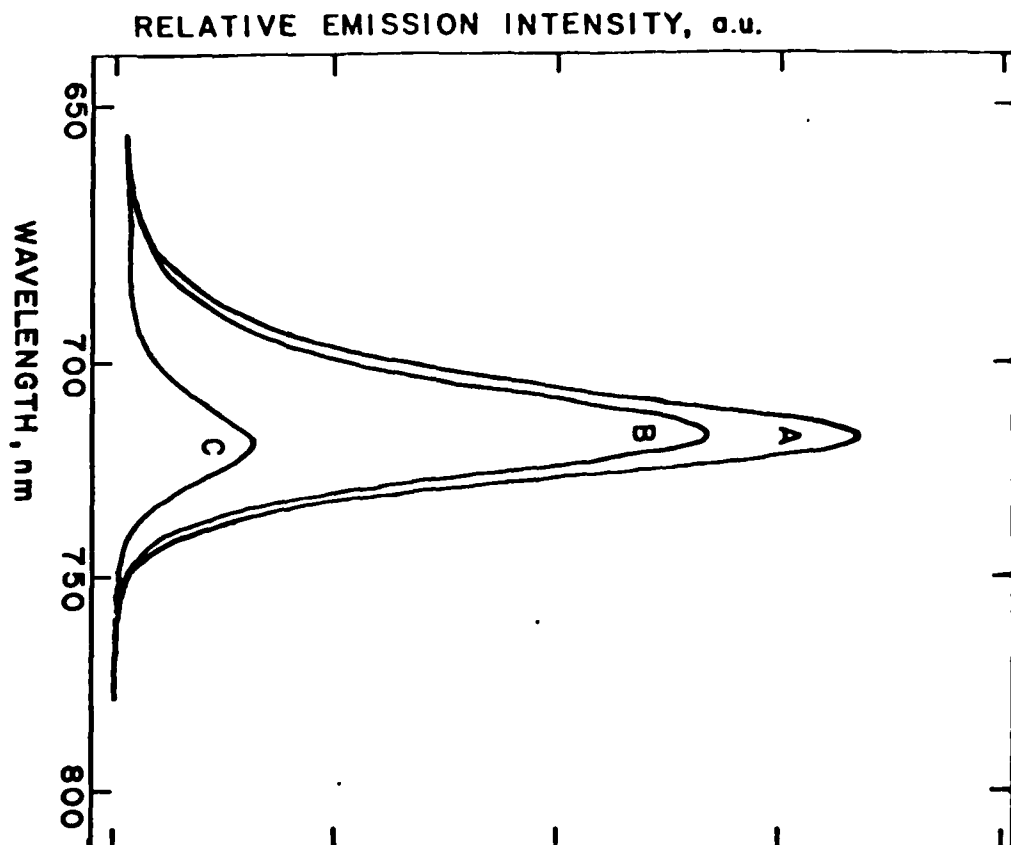
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Figure Caption

Left-hand panel. Uncorrected PL spectrum of a n-CdSe single-crystal electrode excited with 514.5-nm light in a $1\,M\,OH^-/1\,M\,S^{2-}/0.5\,M\,S$ electrolyte. Curves A, B, and C were taken at -1.50 V (open circuit), -1.45 V and -1.30 V vs. SCE, respectively; all spectra were obtained with an identical sample geometry. Right-hand panel. Photocurrent (bottom frame) and emission intensity (top frame) monitored at λ_{max} ~720 nm vs. potential for a n-CdSe single-crystal electrode excited at 514.5 nm in 5 M $OH^-/0.11$ M $Se^{2-}/0.004$ M Se_2^{2-} electrolyte. The photocurrent quantum efficiency, ϕ_x, at -0.3 V vs. SCE was measured to be ~0.9. Related experiments with n-CdSe electrodes are given in ref. 26.

RELATIVE EMISSION INTENSITY, a.u.

WAVELENGTH, nm

650

700

C

B

A

750

800

PHOTOCURRENT, MICROAMPS

0   10   20   30   40   50   60   70

POTENTIAL, VOLTS vs. SCE

-1.5   -1.3   -1.1   -0.9   -0.7   -0.5   -0.3

RELATIVE EMISSION INTENSITY, a.u.

0   10   20   30   40   50   60

CdSe
514.5nm EXCITATION

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